

# Final Report –

## The Abundance and Isotopic Composition of Hg in Extraterrestrial Materials

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During the three year grant period we made excellent progress in our study of the abundances and isotopic compositions of Hg and other volatile trace elements in extraterrestrial materials. At the time the grant started, our collaborating PI, Dante Lauretta, was a postdoctoral research associate working with Peter Buseck at Arizona State University. The work on chondritic Hg was done in collaboration with Dante Lauretta and Peter Buseck and this study was published in Lauretta et al (2001a). In July, 2001 Dante Lauretta accepted a position as an Assistant Professor in the Lunar and Planetary Laboratory at the University of Arizona. His funding was transferred and this grant has supported much of his research activities during his first two years at the U of A. Several other papers are in preparation and will be published soon. We presented papers on this topic at Goldschmidt Conferences, the Lunar and Planetary Science Conferences, and the Annual Meetings of the Meteoritical Society. The work done under this grant has spurred several new directions of inquiry, which we are still pursuing.

### *Bulk Abundances and Isotopic Compositions of Meteoritic Mercury*

Much of our effort was spent developing the methodology to measure the abundance and isotopic composition of Hg at ultratrace levels in solid materials. The analytical techniques for the bulk measurement of trace levels of Hg in solid materials and Hg isotopic compositions have been refined and perfected (see Lauretta et al. 2001a). Bulk chemical abundance and isotopic composition analyses are performed by cold-vapor-generation inductively coupled plasma mass spectrometry (ICP-MS). Relative detection limits are on the order of 0.1 ng/kg, and absolute detectable amounts are ~100 fg. Relative differences in Hg isotopic compositions can be resolved down to  $\pm 0.5$  ‰ on a single-collector (SC-) high-resolution ICP-MS, given sufficient amounts ( $> 1$  µg) of Hg. Using our new multi-collector (MC-) ICP-MS has improved the resolution by an order of magnitude.

In our first study, the abundance and isotopic composition of Hg was determined in bulk samples of the Murchison (CM) and Allende (CV) carbonaceous chondrites (Lauretta et al. 2001a). Prior studies suggested that both meteorites contain isotopically anomalous Hg (Jovanovic and Reed, 1976a,b; Kumar and Goel, 1992). Our measurements show that the relative abundances of all seven stable Hg isotopes are identical to terrestrial values within the precision of our measurements (0.2 - 0.5 ‰) with one exception. The  $^{200}\text{Hg}/^{202}\text{Hg}$  ratio is slightly depleted in Murchison. Work is underway to determine if the observed depletion is significant.

We have continued our study of mercury in primitive meteorites and expanded the suite of meteorites to include other members of the CM and CV chondrite group as well as CI and CO chondrites. Samples of the CI chondrite Orgueil, the CM chondrites Murray, Nogoya, and Cold Bokkeveld, the CO chondrites Kainsaz, Ornans, and Isna, and

the CV chondrites Vigarano, Mokoia, and Grosnaja were gently crushed under ethanol to obtain uniformly-sized powders. The samples were digested in a mixture of HF/HNO<sub>3</sub>/HCl at 210°C/50 bar. Bulk abundance and isotopic composition measurements were performed using an ELEMENT2 (ThermoFinnigan) single-collector magnetic-sector ICP-MS. The isotopic compositions of the meteorites show no significant isotopic anomalies greater than a few permil. These measurements have been repeated by MC-ICP-MS to determine if any fractionation is present below this level. Bulk abundances range from the sub-ppb level up to several ppm (Klaue et al. 2002).

The most exciting results to date have been the discovery of mass-dependent isotopic fractionation among the Hg isotopes in a variety of primitive meteorites, most pronounced in the Vigarano CV chondrite. This is the first verifiable report of isotopic fractionation in this system in extraterrestrial materials. The extent of the fractionation is large with a value of almost 1 permil per mass unit. Mass-dependent fractionation in this system suggests that Hg isotopes can record some of the lowest temperature thermal events that altered primitive solar system material.

### *1.2. Thermal Analysis of Volatile Trace Elements*

We have developed a thermal analysis ICP-MS technique and applied it to the study of a suite of thermally labile elements (Zn, As, Se, Cd, In, Sn, Sb, Te, Hg, Au, Tl, Pb, and Bi) in geologic materials (Lauretta et al. 2001b, 2002a). Depending on the environmental conditions, these elements are either chalcophile or volatile siderophile. It is important to understand how these elements are incorporated and redistributed among sulfide, silicate, and metal phases. Such data could provide constraints on the role that sulfide plays in mantle melting and differentiation, the abundance of S in the mantle, and the processes of accretion and core formation (Yi et al. 2000). Furthermore, these elements may be excellent indicators of both thermal and aqueous processes in the early solar system. The latter has been the focus of our recent research.

Our initial interest in this suite of elements was to gain insight into the low temperature history of primitive meteorites (Lauretta et al. 2001a,b, 2002a). To date we have analyzed 16 different meteorites from the CI, CM, CO, CV, L, LL, and H chondrite groups. Of the entire suite of elements analyzed, only Hg, As, Se, Sb, Te, and (rarely) Cd are released at relatively low temperatures (< 400 °C) from all meteorites studied. The abundances of As, Se, and Te, relative to S, were observed to correlate with the degree of aqueous alteration in the CM chondrites and with oxidation state in the CV chondrites (Browning et al. 1996; McSween 1979). These results suggest that this suite of elements may be useful indicators of aqueous alteration processes on primitive asteroidal bodies. There is also potential for these elements to be used as tracers in terrestrial hydrological studies.

The thermal analysis ICP-MS of trace labile elements has produced some intriguing results (Lauretta et al., 2005). In particular, we have observed a correlation between As, Se, Sb, and Te with low-temperature S release from a wide variety of primitive meteorites. Such a correlation suggests that these elements may also be tracking secondary alteration processes on asteroidal bodies. These elements are predicted to condense as trace elements in troilite (FeS) in the solar nebula. Since they are released from the meteorites at temperatures well below the decomposition temperature for troilite (~988 °C), it is obvious that they have been transferred to a low temperature S-bearing

phase. Furthermore, since their abundance, relative to S, increases with increasing alteration in the CM chondrites, the host phase must be increasing in abundance. Future work will focus on identifying this host phase using scanning electron microscopy coupled with laser ablation ICP-MS. We are also developing a thermodynamic model to constrain the environmental conditions that produce fractionation of As, Se, Sb, and Te between sulfide phases and more oxidized mineral assemblages.

The techniques developed here will be valuable in the analysis of samples returned from the coma of comet Wild-2 by the Stardust spacecraft. We are interested in the abundances of volatile elements in Stardust grains and along particle tracks in the aerogel used to collect these grains. The primary goals of this research are (1) to constrain the initial abundances of volatile elements in Stardust grains and use this information to interpret their origin and thermal history and (2) to determine the amount of heating experienced by Stardust grains during collection. The abundances and isotopic compositions of such elements in Stardust grains may reflect low-temperature gas-solid interactions in the outer, early solar system. We are continuing to develop these techniques using CI and CM chondrites as analogs for cometary particles.

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